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Published in:
Thin Solid Films

DOI:
[10.1016/S0040-6090\(01\)01588-7](https://doi.org/10.1016/S0040-6090(01)01588-7)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

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Citation for published version (APA):

Winder, C., Matt, G., Hummelen, J. C., Janssen, R. A. J., Sariciftci, N. S., & Brabec, C. J. (2002). Sensitization of low bandgap polymer bulk heterojunction solar cells. *Thin Solid Films*, 403-404(7), 373 - 379. [PII S0040-6090(01)01588-7]. [https://doi.org/10.1016/S0040-6090\(01\)01588-7](https://doi.org/10.1016/S0040-6090(01)01588-7)

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Sensitization of low bandgap polymer bulk heterojunction solar cells

C. Winder^{a,*}, G. Matt^a, J.C. Hummelen^b, R.A.J. Janssen^c, N.S. Sariciftci^a, C.J. Brabec^a

^aLinz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University of Linz, Altenbergerstr. 69, A-4040 Linz, Austria

^bStratingh Institute and Materials Science Center, University of Groningen, Groningen, The Netherlands

^cLaboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven,

The Netherlands

Abstract

For efficiently harvesting the terrestrial solar spectrum in conjugated polymer based solar cells, low bandgap polymers with a bandgap <1.8 eV are needed. The photophysics of such low band gap conjugated polymers as well as their excited state interactions with electron acceptors such as fullerenes are of importance when using them in photovoltaic devices. In this work we present a device structural study on the soluble low bandgap polymer PTPTB, consisting of alternating electron-rich *N*-dodecyl-2,5-bis (2'-thienyl)pyrrole (TPT) and electron-deficient 2,1,3-benzothiadiazole (*B*) units. The bandgap of this polymer, determined by electrochemistry and by optical absorption, is 1.6 eV. The performance of the photovoltaic devices is discussed in terms of spectrally resolved photocurrent measurements, AM1.5 measurements and temperature dependent *I*–*V* spectroscopy. Strategies to utilize this polymer for bulk heterojunction tandem solar cells with either a wide band gap polymer or in conjunction with strongly absorbing small molecular dyes are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organic solar cells; Low bandgap polymer; Sensitization; Fullerene and derivatives

1. Introduction

Polymer photovoltaic offers great technological potential as a renewable, alternative source for electrical energy. The demand for inexpensive renewable energy sources is the driving force for new approaches in the production of low cost polymer photovoltaic devices. In the last couple of years, the development of solar cells based on organic molecules [1–3] and conjugated polymers [4–8] has progressed rapidly. Semiconducting polymers in combination with electron accepting fullerenes were found to show an ultrafast photoinduced charge transfer reaction [9,10] at the donor–acceptor interface, which results in a metastable charge-separated state. Utilizing the nanoscopic interpenetrating network of the two constituents (donor/acceptor) in such a ‘bulk het-

erohjunction’ composite allows constructing a large interfacial area and ensures a homogenous, efficient charge generation throughout the sample. Power conversion efficiencies exceeding 2.5% under AM1.5 illumination have recently been reported [4] for bulk heterojunction plastic solar cells [PSC]. One of the limiting parameters in these plastic solar cells is the mismatch of their absorption to the terrestrial solar spectrum. At present substituted poly (*p*-phenylene vinylene)s and polythiophenes are typically used in the construction of PSCs. The optical bandgap of these conjugated polymers ($E_g = 2.0$ – 2.2 eV) is not optimized with respect to the solar emission, which has the maximum photon flux around 1.8 eV. The use of low bandgap polymers [LBG] ($E_g < 1.8$ eV) expands the spectral region of bulk heterojunction solar cells and is a viable route to enhance the number of photons absorbed.

Furthermore, light collection can be improved by using materials which absorbs at different wavelengths, hence of different band gaps.

* Corresponding author. Tel.: +43-732-2468-8767; fax: +43-732-2468-8770.

E-mail address: christoph.winder@jk.at (C. Winder).

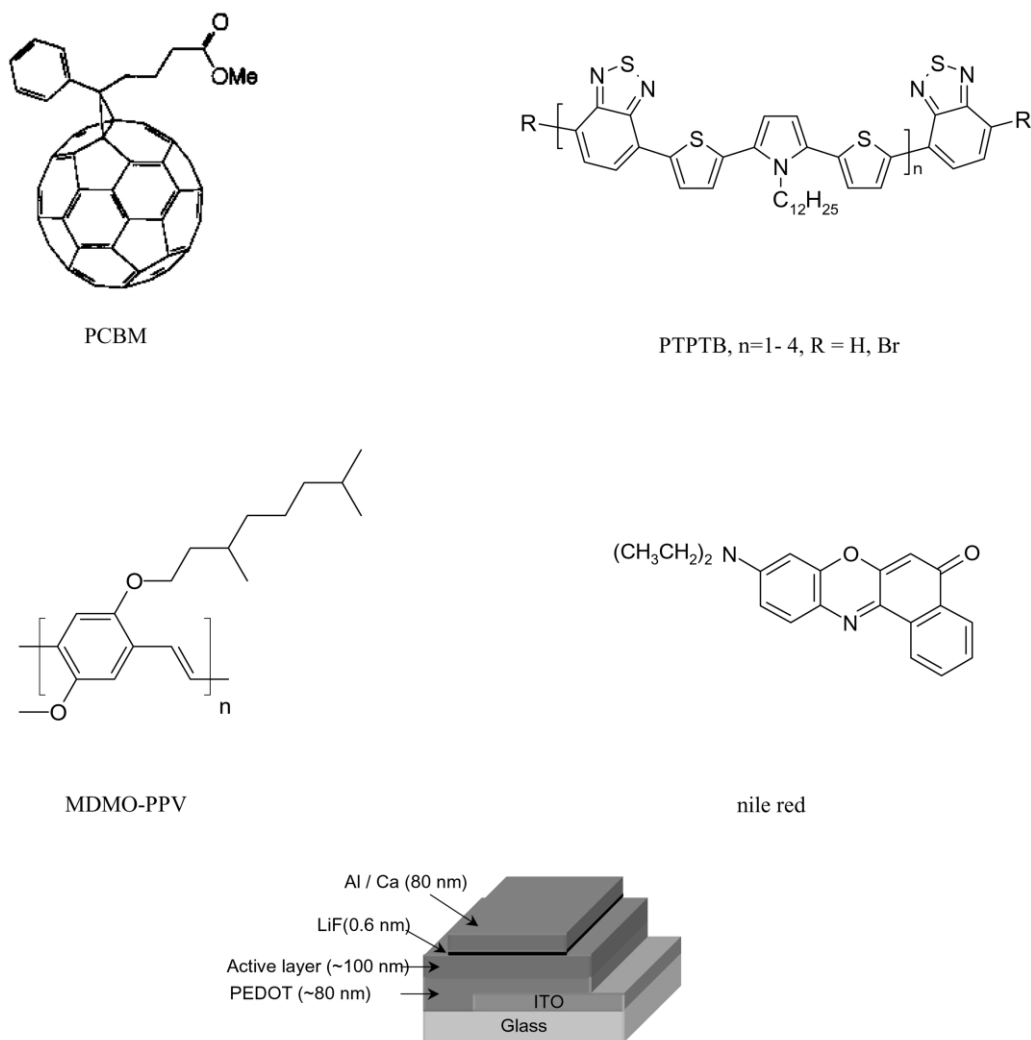


Fig. 1. Chemical Structure of PCBM ([6,6]-Phenyl C₆₁ butyric acid methyl ester), PTPTB (Poly-*N*-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole), MDMO-PPV [poly (2-methoxy, 5-(3,7-dimethyloctyloxy)) para phenylene-vinylene] and Nile red (9-(Diethylamino)-5H-benzo[*a*]phenoxazin-5-one).

Bulk heterojunction devices offer an easy approach via blending different conjugated polymers of different bandgaps or different organic dyes with conjugated polymers.

In this paper, we will present results for the new low bandgap polymer PTPTB cells as well as first results for solar cells with the addition of either a wide bandgap polymer or an organic dye as antenna for light collection. First promising experiments are shown and the upcoming problems in this new type of blended solar cells are discussed.

Polymer LEDs, on the other hand, are already entering display markets and large effort in this area is dedicated by optoelectronics manufacturers worldwide. A traditional important wavelength area for LED devices is the near infrared (NIR) where the telecommunication frequency windows are located. A polymer LED in these NIR frequencies would be important as pump source for

telecommunication devices. Reports on IR emission from conjugated polymers are rare [11,12] due to the lack of materials. Therefore, the possibility of obtaining a light source working at telecommunication wavelengths and/or for medical treatment applications, together with the functionality of the same material for photovoltaic devices as demonstrated in this work is promising.

2. Experimental

The structure of the devices and the materials used in the active layer is shown in Fig. 1. Devices were produced on ITO/glass substrates. The ITO was cleaned in an ultrasonic bath using acetone and subsequently isopropanol as cleaning solvent. A layer of poly(ethylene dioxythiophene) doped with polystyrene sulphonic acid (PEDOT:PSS, Bayer AG) was spincoated

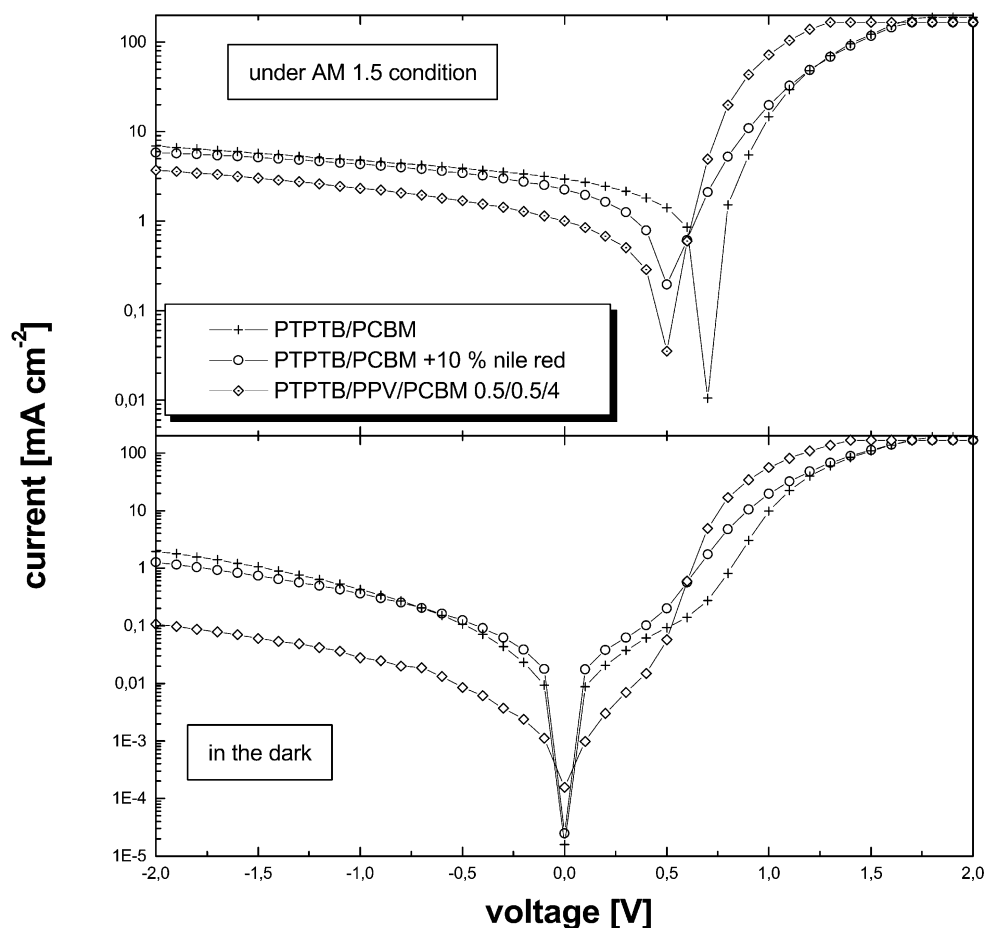


Fig. 2. I - V curves under AM1.5 conditions (upper part) and in the dark (lower part) for a device with PTPTB/PCBM 1/3 (—+—), PTPTB / PCBM 1/3 + 10% Nile red (—o—), and PTPTB/MDMO-PPV/PCBM 0.5/0.5/4 (—◇—).

from an aqueous solution on the ITO substrate, giving a thickness of ~ 100 nm. PEDOT:PSS is widely used in organic electronics in order to smooth the ITO surface and to improve the hole injection at the ITO anode.

The PTPTB/PCBM layers and the PTPTB/PCBM/nile red layers were spincoated from toluene solutions. The MDMO-PPV/PTPTB/PCBM and the PTPTB layers for the electroluminescence measurements were spincoated from chlorobenzene solutions. The average thickness of the active layers, determined by AFM measurements, was between 80 and 110 nm.

For the negative electrode, a two-layer deposition of LiF/Al was used. This technique has been shown to enhance the charge injection at the interface between the active layer and the cathode in organic light-emitting diodes [13,14]. A small amount of LiF was first thermally deposited (10^{-4} Pa) with an average thickness of 0.6 nm onto the active layer and finally, the aluminium cathode was thermally deposited (60 nm) through a shadow mask to define a device area of 5 mm^2 .

I - V curves were measured under 80 mW/cm^2 white

light illumination from a Steuernagel solar simulator (metal halogenide lamps with AM1.5 filters) to simulate AM1.5 conditions. The spectral photocurrent was detected by a Lock-In amplifier while the sample was excited with monochromatic light. The light is chopped with a frequency of 276 Hz.

The electroluminescence was measured with an Avantes spectrometer. The spectra are corrected for the detector sensitivity. All device characterisation was done under inert argon atmosphere. AFM measurements are done with a Dimension 3100 instrument from Digital Instruments, Santa Barbara, CA, in the tapping mode.

For low temperature studies, cells with pristine MDMO-PPV and MDMO-PPV/PTPTB 1:1 (wt.%) with Au electrodes were produced. Au has a high work function and should therefore be a good hole injection contact and provide a high barrier for electron injection. The device will, therefore, be a hole-only device as described by Blom and Vissenberg [15]. The cells were cooled down to liquid helium temperature and I - V curves were recorded during heating up. Room temper-

Table 1
PV performance parameter of the devices under AM1.5 conditions

Active layer	V_{OC} (V)	I_{SC} (mA/cm ²)	FF	R (± 1 V) (dark)	η_e (AM1.5) (%)
PTPTB/PCBM 1/3	0.72	2.95	0.37	23	0.1
PTPTB/PCBM + 10% Nile red 1/3	0.53	2.25	0.32	55	0.48
PTPTB/PPV/PC BM 0.5/0.5/4	0.51	1.0	0.3	2008	0.2
PPV/PCBM 1/4	0.81	4.9	0.6	140	3.0

ature curves were recorded before and after the cooling to monitor possible damage of the device. The cells showed in all cases the same characteristic before and after the measurement.

3. Results and discussion

Fig. 2 shows the I - V curves of a bulk heterojunction device from PTPTB/PCBM (1:3 wt. ratio). The low rectification of the device ($\sim 10^2$ at ± 2 V) reflects the rather poor film forming properties of PTPTB, which are induced by the low average polymer length distribution (5–16 aromatic units as determined from size exclusion chromatography). Under simulated AM1.5 illumination, a strong photoeffect is observed in the I - V curve. The open circuit voltage of 0.72 V is just 0.1 V less than in the highest values observed for MDMO-PPV/fullerene devices although the bandgap of PTPTB

is reduced by 0.6 eV compared to MDMO-PPV. The observation of similar open circuit voltages for devices with identical acceptors but polymers with different HOMO levels (~ 0.4 eV offset) indicates an influence of the metal electrode (ITO/PEDOT) on the electrical potentials at the positive electrode/semiconductor interface. Therefore no limitation in the use of low bandgap materials in polymer solar cells can be seen as long as the proper electrodes are provided. The short circuit current I_{SC} is measured with 3 mA/cm² and the fill factor FF is calculated to be 0.37. From these values, the power conversion efficiency $\eta_{AM1.5}$ is calculated to be $\sim 1\%$. The photovoltaic parameters of all devices are also summarized in Table 1.

While the short circuit current of the device is already satisfyingly high, the overall efficiency of the device is limited by the low fill factor. Generally, low FF can be

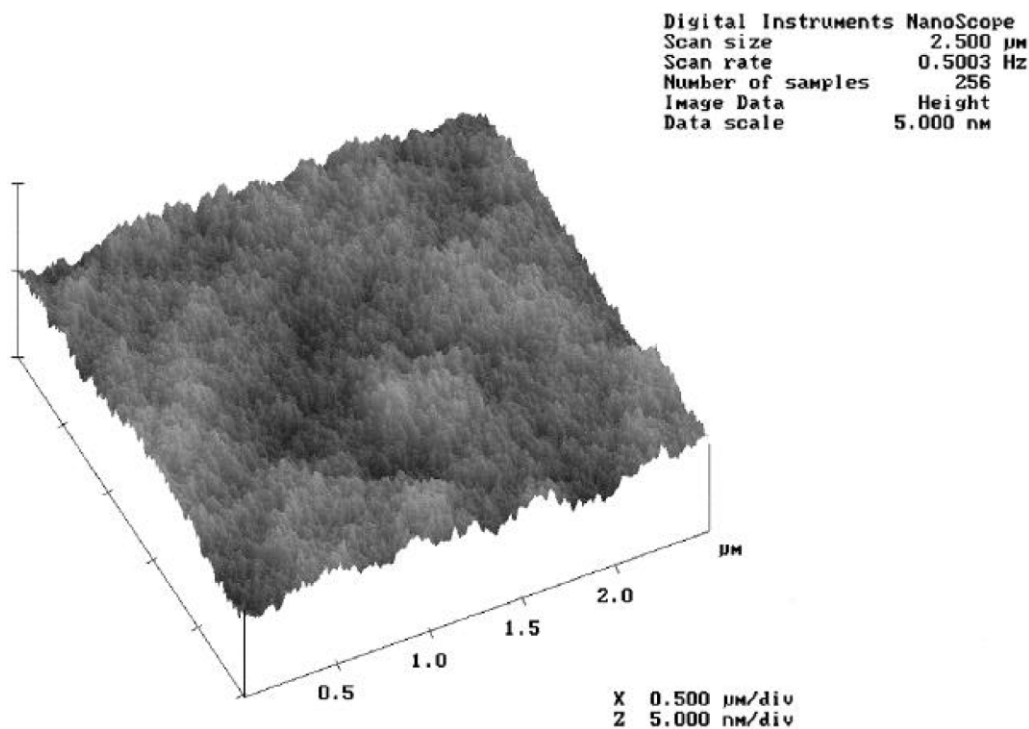


Fig. 3. AFM picture of PTPTB/PCBM 1/3 blend with highest efficiency. AFM in tapping mode.

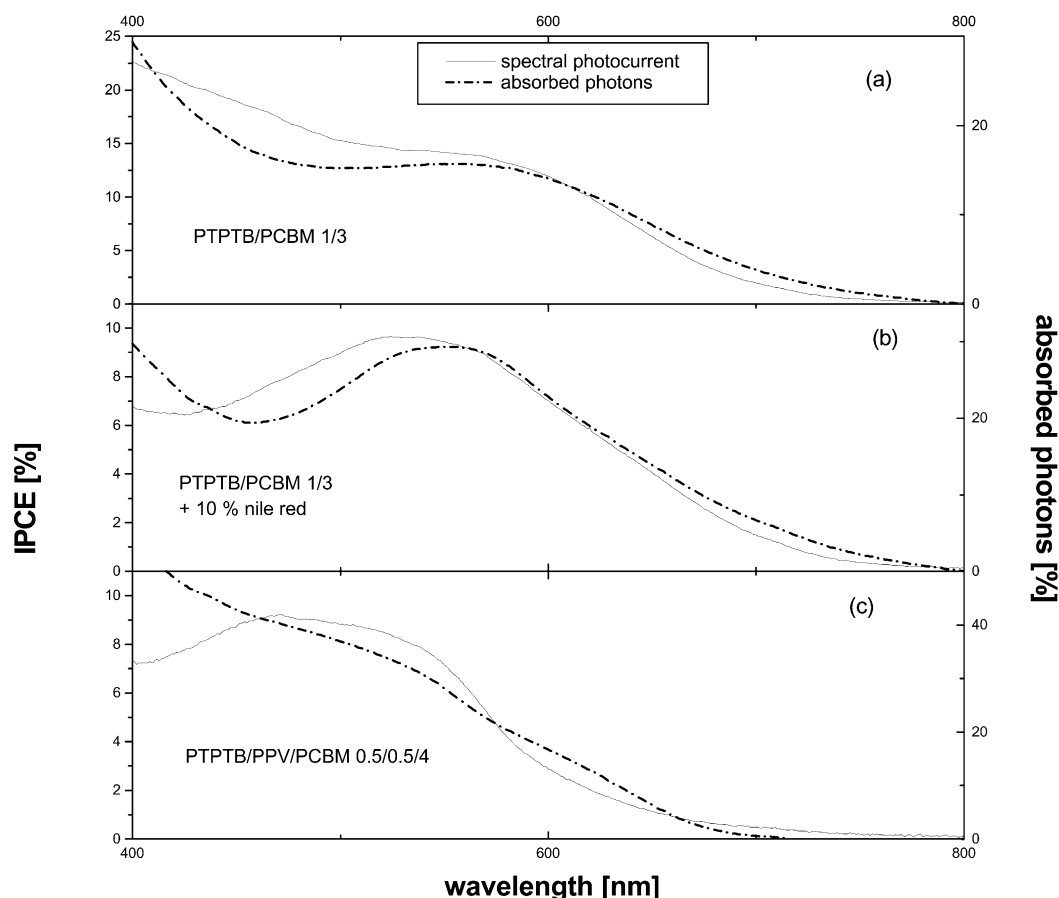


Fig. 4. Spectral resolved photocurrent (IPCE) (—) and absorbed photons (---) of the active layer (measured in transmission) of (a) PTPTB/PCBM 1/3, (b) PTPTB/PCBM 1/3 + 10% Nile red, (c) PTPTB/PPV/PCBM 0.5/0.5/4.

induced by high series resistances or by small shunt resistances. For PTPTB/PCBM devices we find series resistances below $10 \Omega/\text{cm}^2$, which cannot explain the low FF. Therefore, the low FF is expected to originate from a small parallel resistance in the device. The nature of the shunt is still under discussion, but AFM measurements (Fig. 3) on the surface of the photoactive layer show films with a surface roughness of around 5 nm, i.e. one order in magnitude higher than observed for MDMO-PPV/PCBM devices [4]. Most likely, the low molecular weight of the polymer, together with partial phase incompatibility between PTPTB and PCBM induces the low film quality. Other mechanisms responsible for the reduction of the FF include field dependent recombination processes, probably induced by the energetically close positions of PTPTB^- and PCBM^- , thereby reducing the selectivity of the negative contact to separate holes and electrons.

Fig. 4a shows the spectral resolved photocurrent IPCE and the amount of absorbed photons in comparison. The spectral photocurrent of the PTPTB/PCBM peaks at 600 nm and contributions to the IPCE are observed down to 750 nm, evidencing the low bandgap of PTPTB.

Upon blending 10 wt.% of a highly absorbing, small molecular dye (Nile red) into the photoactive PTPTB/PCBM blend, no major changes are observed in the dark I - V characteristics (Fig. 2). Only the onset for the injection in forward direction is slightly lowered. Under illumination, the open circuit voltage is found to be reduced from 0.72 to 0.53 V upon addition of the dye. The photoactivity of the dye is evidenced by the spectral photocurrent measurements (Fig. 4b). Both, the maximum of the spectrally resolved photocurrent and of the absorption are shifted to 550 nm, i.e. the absorption maximum of the dye. The contribution of PTPTB to the photocurrent is still in the region between 600 and 750 nm, which is strikingly similar shape as the PTPTB/PCBM device. Although we can show, that both absorbing compounds, the conjugated polymer and the small molecular dye contribute to the photocurrent, the overall performance of the device is slightly lowered. The primary photoreaction in this three component system, either energy transfer from Nile red to PTPTB and subsequent electron transfer from PTPTB to PCBM vs. mutual electron transfer from both absorbers (Nile red and PTPTB) to PCBM is still under investigation. It is

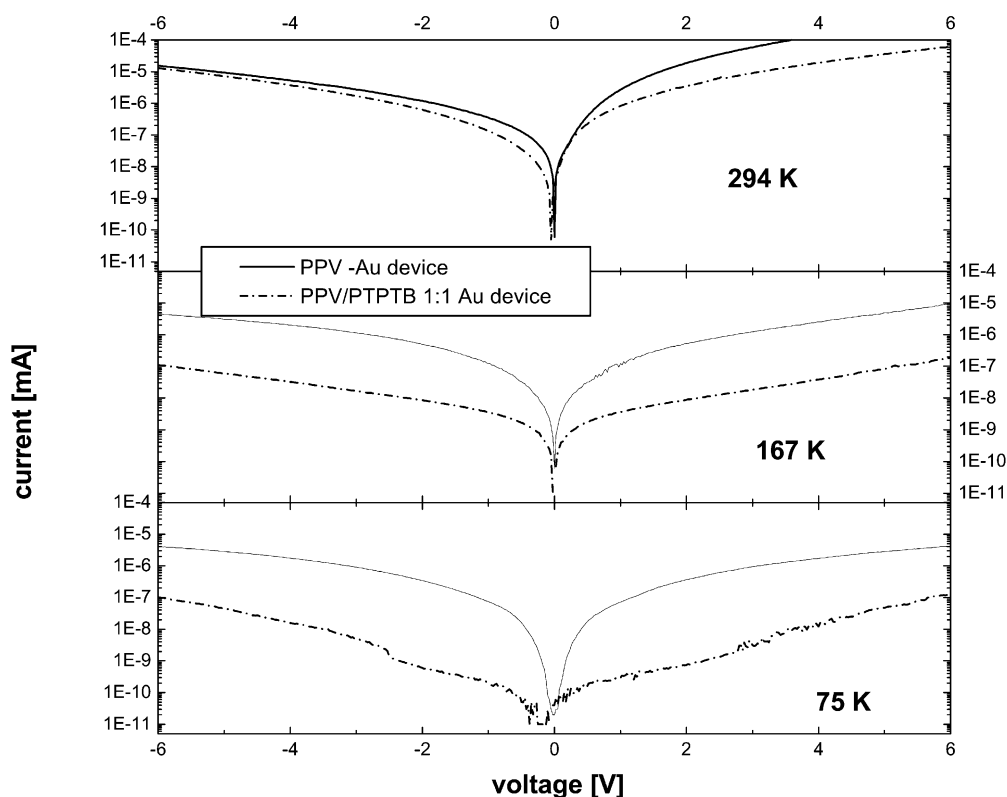


Fig. 5. I - V curves in the dark of a ITO-PEDOT/PPV/Au device (—) and a ITO-PEDOT/PPV-PTPTB 1:1/Au device (---) at 296 K (upper layer), 167 K (middle layer) and 75 K (lower layer), the thickness of both devices is determined with ~ 115 nm by AFM tapping mode.

clear however, that positive charges on Nile red photo-generated in the second reaction pathway would demand at least one additional transport step via a possibly inefficient hopping process.

A blended composite of MDMO-PPV, PTPTB and PCBM in a weight ratio of 0.5:0.5:4 is used as photo-

active layer to investigate the polymer mixture approach. The beneficial effect of mixing MDMO-PPV into the PTPTB/PCBM composite on the diode quality (Fig. 2b) is demonstrated by a higher forward and a lower reverse current. Overall, this leads to an increase in the rectification for this device by more than an order in

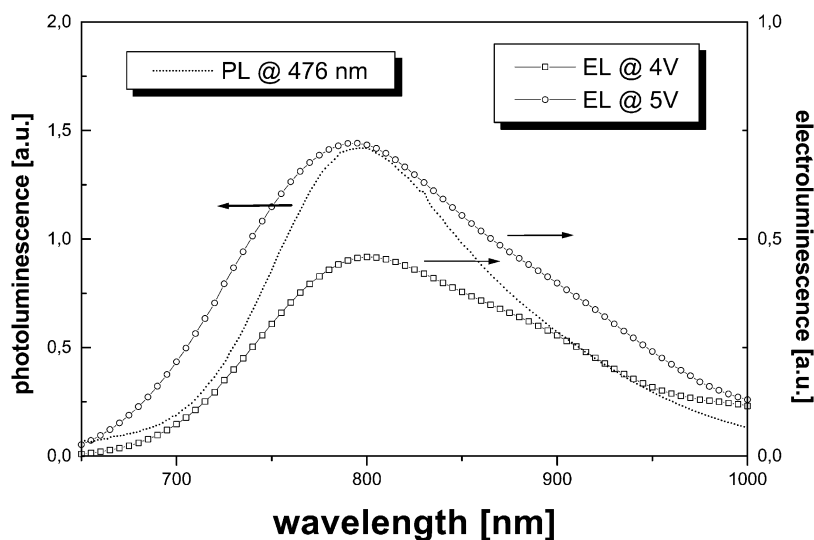


Fig. 6. Photoluminescence (---), excited with 40 mW laser at 476 nm, of PTPTB and electroluminescence of a pristine PTPTB device at 4 V (□-) and 5 V (-○-).

magnitude. However, under illumination this device shows reduced V_{oc} , I_{sc} and even FF as compared to the PTPTB/PCBM reference device. The spectral resolved photocurrent of the polymer mixture device (Fig. 4c) is dominated by the contribution of MDMO-PPV approximately 500 nm, and only weak near IR part might be attributed to PTPTB. Interestingly, the shoulder in the absorption spectrum approximately 600 nm, originating from PTPTB, has no pendant in the spectral photocurrent. Obviously, in the blend, excited PTPTB does not contribute to the photocurrent in the same extent like MDMO-PPV.

In order to understand the performance of the tandem device, we studied the transport processes of pristine MDMO-PPV and in composites with PTPTB. ITO/PEDOT and Au electrodes were chosen to guarantee hole only devices. The dark I - V curves of the two devices are compared at different temperatures in Fig. 5. For pristine MDMO-PPV, the same results could be found like Blom and Vissenberg [15]. At room temperature, the forward current scales with V^α , where α is > 2 , indicating space charge limiting current (SCLC) transport in the presence of traps [16]. At lower temperatures (167 and 75 K), electron contributions to the current are frozen out and trap free SCLC transport is observed ($\alpha \sim 2$), allowing to estimate a hole mobility of $\sim 10^{-6} \text{ cm}^2/\text{V}^1 \text{ s}^{-1}$ for $T < 200 \text{ K}$. For the composite even at that low temperature trap free SCLC is not observed. We suggest, that the reduced PV performance of the polymer mixture devices origin is in the low hole mobility and the presence of hole traps in the composite.

Finally, we want to demonstrate the large potential of PTPTB for optoelectronic applications beyond solar cells. Using pristine PTPTB as active layer for an

organic light emitting diode, near IR electroluminescence with an onset approximately 3 V is observed (Fig. 6).

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